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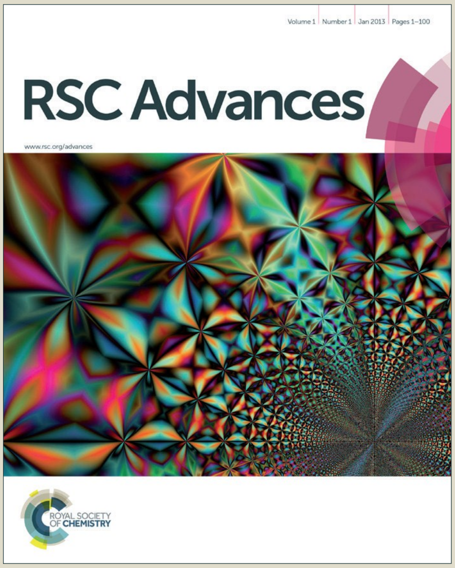

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High proton conductivity sulfonated methoxyphenyl-containing poly(arylene ether ketone) for proton exchange membrane

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Abstract

A series of the sulfonated methoxyphenyl-containing poly(arylene ether ketone) (SMP-PAEK) were synthesized via polycondensation from 2-(3-methoxy)phenylhydroquinone and other commercial monomer, following by postsulfonation approach under mild reaction conditions. Controlled substituted sites and the degree of sulfonation were realized by using quantities of 2-(3-methoxy)phenylhydroquinone. Given sulfonated polymers (SMP-PAEK) can be soluble in common organic solvents such as DMSO, NMP, and DMAc. The tough and transparent polymer membrane was prepared by solution casting method, exhibited excellent mechanical properties and high proton conductivities. The tensile stress at maximum load and elongation at break of these membranes are 30.0-32.4 MPa, and 120-171% in dry state respectively. The proton conductivities of these membranes are higher than that of Nafion 117 in water. Especially the SMP-PAEK-80 with IEC of 1.62 mequiv/g exhibited the highest proton conductivity of 294 mS/cm at 80 °C in water. In addition, SMP-PAEK-90 with IEC of 1.83 mequiv/g exhibited suitable proton conductivities in different relative humidity (RH) (30~98%) at 80°C, which is higher than Nafion 117. The clear micro-phase separation morphology was observed by SAXS, which is a powerful evidence to explain their high conductive behaviors. In addition, the current density of the SMP-PAEK-80 membranes was measured to be 235 mA/cm^2 at 0.36 voltage (V) under fully hydrated conditions at room temperature with a 1.5bar back pressure in a MEA cell performance test.

1. Introduction

Fuel cell technology is expected to become one of the key technologies of the 21st century both for stationary applications like block power station and personal vehicles. Proton exchange membrane fuel cells (PEMFC) are attracting considerable attention because of their high energy density and efficiency, low emissions, and various applications such as in residential power generation, portable electronics and electric vehicles.[1-4] The proton-exchange membrane (PEM) is the key component which affects the performance of a fuel cell system because only highly stable membranes can withstand the harsh chemical and physical environment in a fuel cell. The required properties for PEMs are high proton conductivity, low methanol crossover, long-term stability and low cost.[5, 6] Currently, most widely used proton exchange membranes are based on water-swollen polymer electrolyte membranes containing sulfonic acid groups (*e.g.* Nafion-based perfluorinated ionomer polymer) they owning outstanding chemical stability and excellent performance, including excellent proton conductivity, mechanical strength, and electrochemical resistance to membrane decomposition. However, they suffer from several shortcomings among which their high cost presents a major obstacle for widespread application in PEMFC. In addition, a loss of proton conductivity above 80 °C and low resistance toward alcohols cross-leaks impose restrictions on the operating temperature and choice of possible fuels.[7] Therefore, searching for alternative PEMFC materials is of importance. the proton exchange membrane (PEM) must possess several characteristics including high proton conductivity, low electrical conductivity, low permeability to fuel and oxidant, oxidative and hydrolytic stability, balanced water transport, good mechanical properties, and the capability to be assembled into a membrane electrode assembly (MEA) at low cost.[8] Alternative membranes have been developed by adopting sulfonated aromatic hydrocarbon structure such as poly(arylene ether sulfone)s,[9,10] poly(ether ether ketone)s, [11–13] poly(sulfide sulfone)s,[14] polyimides,[15] polyphosphazenes, [16] polybenzimidazoles [17] and polyphenylenes [18].

Almost all aromatic hydrocarbon structure polymers containing sulfonic acid groups are typically prepared either by postsulfonation reaction or direct polymerization reaction of sulfonated monomers. From the molecular design point of view, direct copolymerization of sulfonated monomers with other nonsulfonated aromatic monomers can ensure a better control of the degree of sulfonation (DS) and the polymer chain structure [19-21]**.** However, direct polymerization is not susceptible to possible side reactions such as degradation and cross-linking which could occur in strongly acidic media usually used for postsulfonation[8,22-26], and available sulfonated monomers are very limited and high-molecular-weight enough ductile membranes can be achieved only when reactive another monomers are used. Moreover, sulfonated aromatic monomers are less reactive in comparison with non-sulfonated ones and are subjected to undergo side reactions at higher temperature (for example, the temperature of PAEKs synthesis is at 170-180 °C). Compared to direct polymerization, high-molecular-weight polymer electrolytes can be more easily realized in a postsulfonation method because of highly reactive unsulfonated monomers. The flexible choice of monomers is another great advantage of the postsulfonation method. Therefore, aromatic PEM prepared by postsulfonation is more suitable for the requirement of practical application than it by direct copolymerization. Because postsulfonation is much simpler, faster, easier, and cheaper than the sulfonation of the monomer followed by a polymerization step. However, the polymer hydrophobic blocks have to be carefully designed not to be sulfonated during postsulfonation reactions so as to achieve hydrophilic/hydrophobic stable microphase structures, and keep good mechanical properties when it operating high relative humidity and (or) high temperature.

In the past decade, the researcher spend much effort on improve hydrophilic/hydrophobic microphase separation structures for aromatic PEM. For example, Miyatake group reported on a method to control the sulfonation sites by adjusting the molecular structures of the host polymers[27]. The constructing of sulfonation groups onto polymer side chains induce strong phase separation between the hydrophobic main chain and the hydrophilic side chain. This phase separated morphology can decelerate polymer main chain degradation by radical species that are present in the water channel. The McGrath group first introduced fluorine groups into hydrocarbon PEMs using 4,4-hexafluoroisopropylidene bisphenol (6F-BPA) monomers for SPAES copolymers[28]. The authors studied the effect of bisphenol monomers with various chemical structures on the properties of the resulting SPAES copolymers, 6F-BPA copolymer systems exhibited the lowest water sorption due to the hydrophobicity of the fluorine groups. Guiver group expanded the above concept to first prepared sulfonated poly(aryl ether ketone)s (Ph-6FA-SPEEK) containing hexafluoroisopropylidene diphenyl moieties by postsulfonation under mild reaction conditions. The sulfonated polymer with controllable DS and sulfonation sit are exhibited excellent mechanical properties and good chemical and dimensional stability even at high temperature. This attributed they have optimized molecular structure which bearing in stable hydrophilic/hydrophobic microphase structures. But unfortunately, the proton conductivity of Ph-6FA-SPEEK still lower than that of Nafion 117.

As one of the most impotent aromatic PEM, Sulfonate poly(arylene ether ketone)s (PAEKs) a have been extensively studied [29–33]. The major current challenge in ion exchange membrane development is how to improve the proton conductivity of the membrane, meanwhile, not to sacrifice the mechanical property, dimensional stability and methanol permeation of the membrane materials because of excessive swelling, especially postsulfonated PAEK membrens. To date, incorporation of various chemical moieties and postmodification reactions of SPAEKs have been investigated.[34–37] However, to our knowledge, they have synthesized a series of SPAEKs polymers which possess low proton conductivity. Thereby affected the single cell performance for the membrane. Therefore, numerous approaches have been taken to reduce swelling of membrane materials without sacrificing the proton conductivity as much as possible. In the present work, we synthesized a series of PAEKs containing sulfonated methoxyl phenyl pendent (SMP-PAEK), and hydrophobic mainchain via a postsulfonation method under mild reaction conditions.

Here, the incorporation of the larger rigid 6FBPA moiety into the backbone is an attempt to increase the hydrophobicity and length of nonsulfonated segments and to improve the membranes' mechanical properties as well as the thermal stability of SPAEK. The 6FBPA unit also enhances the polymers' solubility and film-forming ability. And the sulfonation reaction only occur in ortho-position of methoxyl group in side chain under the sulfonation condition because of active methoxyphenyl group side chain. The structure and some properties of the synthesized polymers were studied with particular emphasis on the PEM-related properties. The SMP-PAEK membranes exhibited excellent mechanical properties, high proton conductivities and good single-cell performance.

2. Experimental Section

2.1 Materials

3-Methoxyanilione and benzoquinone were purchase from Shanghai Chemical Company. 4,4'-Difluorobenzophenone (DFBP) (purity, >99.0%) and 4,4'-(Hexafluoroisopropylidene)diphenol (6FBPA) (purity, >99.0%) were purchase from Beijing Chemical Company. Other commercially available materials and solvents were used without further purification.

2.2 Synthesis of 2-(3-methoxyphenyl)hydroquinone

The bisphenol monomer, 2-(3-methoxy)phenylhydroquinone (MeOPHQ) was synthesized according to the literature.[38] The pure bisphenol was obtained as white crystal after recrystallization from water and dried in a vacuum oven at 80 oC for12 h.

MP: 136 ^{o}C (DSC).

IR (cm^{-1}): 3403 (–OH), 2832 (–CH_3), 1225 (–O–), 3050 (Ar–).

^{1}H NMR (500 MHz, DMSO-d_6, δ): 8.75 (s, 1H), 8.73 (s, 1H), 7.28 (t, J = 8.5 Hz, 1H), 7.05 (m, 2H), 6.84 (m, 1H), 6.73 (d, J= Hz,1H), 6.66 (d, J =3.0 Hz, 1H), 6.66 (d, J = 9.0, 3.0, 1H), 3.77 (s, 3H).

2.3 synthesis of polymers

A series of methoxyphenyl poly(arylene ether ketone) (MP-PAEK) were successful prepared. As shown in scheme 1, The polymers containing 60%, 70%, 80%, 90% methoxyphenyl content were synthesized from 2-(3-methoxyphenyl)hydroquinone, 4,4'-difluorobenzophenone and 4,4'-(hexafluoroisopropylidene) diphenol (6FBPA).With the polymer containing 60% meta-methoxyphenyl as an example to introduce the synthesis and post-processing of polymer: To a three-necked flask with an agitator, a nitrogen inlet a Dean-Stark trap with a condenser were added 2-(3-methoxyphenyl)hydroquinone (0.006 mol, 1.2879 g), 4,4'-difluorobenzophenone（0.01 mol, 2.1820 g）, 6FBPA（0.004 mol，1.3449 g）, anhydrous K_2CO_3 (0.011 mol, 1.52 g), tetramethylene sulfone (TMS) (15.3 mL), and toluene (15 mL) were loaded.The system was allowed to reflux for 2 h, and then the azeotrope of toluene with water was removed. The reaction mixture was heated to 175 °C. After 6 h, the viscous solution was poured into water. The polymer was refluxed in deionized water and ethanol several times to remove the salts and solvents and was dried in a vacuum oven at 100 ^{o}C for 12 h. All the other starting polymers were prepared using the same synthesis and purification routine.

2.4 Preparation of Sulfonated Polymers and Their Membranes.

In view of high substitution reactivity of the pendant methoxyphenyl groups, a relatively mild sulfonating reagent and ambient temperature conditions were adopted. A typical reaction was shown as follows:

To a 100 mL of flask, 1 g of MP-PAEK and 15 mL of concentrated sulfuric acid (95-98 %) were added. After stirring at room temperature for 12 h, the homogeneous viscous solution was poured into a mixture of water and ice to get a silklike solid. The solid was washed with water and until the water reached neutral, then washed three times by ethanol. The sulfonated MP-PAEK (recorded as SMP-PAEK) was dried in a vacuum oven at 120 °C for 12 h.

IR (cm^{-1}): 1651 (C=O), 1030, 1078, 1095, ($-SO_3H$)

^1H NMR (500 MHz, DMSO-d_6, δ):8.26 (d, 1H), 7.76 (d, 1H), 7.7 (d, 1H), 7.68 (s, 1H), 7.55 (d, 1H), 7.42 (d, 1H), 7.28 (d, 1H), 7.18 (d, 1H), 6.7 (s, 1H).

SMP-PAEK (1 g) in DMAc (10 mL) solution was cast onto a flat glass plate. Drying the solution in vacuum oven for 12 h at 120 °C, obtained a 70-80 μm thick, transparent, and tough film. The membrane was immersed in 2 M H_2SO_4 aqueous solution for 12 h, washed with water several times and dried at 120 °C.

2.5. Water uptake

A piece of film(1cm×4cm) was vacuum dried at 120 °C to a constant weight and length, which is recorded as W_{dry} and $L_{dry,}$ and then immersed in deionized water or keep in water vapor with different RH for 24h until equilibrium status. During this period, the wet membrane was quickly measure weight or length several times, which was recorded as W_{wet} and L_{dry}. The water uptake and swelling ratio were reported using water weight percent and length percent of dry membranes as following relation:

$$\text{Water uptake}=[(W_{wet}-W_{dr})/W_{dry}]\times 100\%$$

$$\text{Swelling ratio}=[(L_{\mathrm{wet}}-L_{\mathrm{dry}})/L_{\mathrm{dry}}]\times 100\%$$

2.6. Thermal stability

Thermal stability of the membranes was analyzed using differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) The glass transition temperatures (T_g) were obtained on a Mettler-Toledo DSC821^e differential scanning calorimeter. Scans were conducted under nitrogen at a heating rate of 10 °C/min. Second heat T_g values are reported as the midpoint of the change in the slope of the baseline. Dynamic TGA was employed to assess the thermal stability (weight loss) of the copolymers with a Pyris 1 TGA (Perkin Elmer) thermogravimetric analyzer. All the samples were first vacuum dried and kept in the TGA furnace at 150 °C in a nitrogen atmosphere for 20 min to remove water before TGA characterization. The typical heating rate was 10 °C/min in air. The 5% of mass loss of thermal decomposition temperature ($T_{d\ 5\%}$) was used to assess the thermal stability of polymers

2.7. Degree of sulfonation (DS) and Ion exchange capacity (IEC)

SMP-PAEK is a copolymer that has a sufonated unit and nonsulfonated unit. The DS can thus be defined as:

$$DS=A/(A+B)$$

where A and B are the molar numbers of the sulfonated unit and nonsulfonated unit, respectively.

The DS and IEC can be calculated from the sulfur content determined by elemental analysis on Vario EL cube using CHNS mode. As calculated by formula:

$$DS= 514S/[32+(514-474)S]$$

$$^{a}IEC(mequiv/g)= 100S/32$$

where S is the sulfur content (wt %) in the polymer, and 514, 32, and 474 are the molecular weights of the sulfonated unit, sulfur and the nonsulfoated unit, respectively.

The titration technique also was used to determine the IEC of the membranes. Firstly, the membranes in the acid form (H+) were converted to the sodium form by immersing the membranes in a 1M NaCl solution for 24 h to exchange the H^+ ions with Na^+ ions. Then, the exchanged H+ ions within the solutions were titrated with a 0.01M NaOH solution.

IEC was calculated by formula:

$$^{b}IEC(mequiv/g)=(V_{NaOH}\times C_{NaOH})/(W_{dry})$$

Where V_{NaOH} (mL) is he volume of NaOH solution, C_{NaOH} (mol/L) the concentration of NaOH solution, W_{dry} (g) the weight of polymer.

2.8. Proton conductivity

A sheet of sulfonated membrane (1cm×4 cm) was placed in a test cell similar with previous reports and this cell geometry was chosen to ensure that the membrane resistance dominated the response of the system.[39] Proton conductivities of hydrated membranes were measured using a complex impedance analyzer (AC impedance spectroscopy, Princeton Applied Research PARSTAT 2273) over a frequency range of 1–10,0000 kHz. Temperature in the range of 20-100 °C. During testing the humidity was kept at 100%, and keep in water vapor with different RH. The impedance measurements were performed in water vapor with different RH at 80 °C. Before measurement, the films were hydrated in different relative humidity for 24 h. The proton conductivity was calculated by formula

$$\sigma = L/RA$$

where σ is the proton conductivity, L the membrane thickness, R the membrane resistance and A is the membrane area.

2.9 PEMFC single cell performance

For the membrane electrode assembly (MEA) fabrication, 20 wt% Pt/C (Alfa Aesar, MA, USA) and 20 wt% Nafion ionomer (Sigma Aldrich, MO, USA) were used as a catalyst and binder, respectively. The catalyst was loaded onto a gas diffusion layer containing a microporous layer with an overall Pt loading amount of 0.5 mg/cm^2 The membrane was sandwiched between two catalyst coated substrates and then hot-pressed at 130 ^{o}C and 20 bar for 5 min. PEMFC single cell performances were measured using a fuel cell test station (CNL, Korea). The fuel cell tests were carried out under fully hydration condition at 80 ^{o}C with a backpressure of 1.5 bar. Hydrogen for an anode and air for a cathode was fed into a single cell at a rate of 100 mL/min and 300 mL/min as the fuel and oxidant, respectively. The change of current density (active area is 9 cm^2) was observed by loading the voltage, and the power density was calculated from the voltage and current density.

2.10. Small angle X-ray scattering

All the measurements were carried out at room temperatures with a Small-angle X-ray scattering system (SAXSess mc2) with sealed tube X-ray generator. The wavelength (l) is 0.1542 nm. Hydrated membranes were analyzed in a solid sample holder at 25 °C. The range of scattering vectors explored ($q = 4\pi \sin 2\theta/\lambda_i$) was from 0.085 to 3.0 nm^{-1}, where λ_i and 2θ are the incident wavelength and total scattering angle, respectively. The characteristic separation length *d* (nm), i.e. the Bragg spacing, was calculated using

$$d=2\pi/q.$$

2.11 Mechanical property

The mechanical properties of membranes in wet status were detected on a SHIMADIU AG-I 1KN electromechanical universal testing machine. The stretching dimensions of the sample were 15 mm × 4 mm, and the tensile speed was 2mm min^{-1}, each sample repeated three times, took the average. Before testing the membranes were immersed in water for 24h until equilibrium status at room temperature.

3. Results and discussion

3.1 Synthesis and sulfonation of polymer

Sulfonated poly(arylene ether) polymer that possess precise control of the sulfonation sites and the degree of sulfonation was obtained by postsulfonation method, it is to be expected that the structure of polymer was constructed from stable backbone and active side chain. As shown in scheme 1, the main chain that contain electron-deficient phenyl rings was synthesized from 4,4'-difluorobenzophenone, and 6FBPA, and it was stable in concentrated sulfuric acid at room temperature.[39] Conversely, methoxyphenyl pendent groups which connect on side chain exhibited higher activity. A series of SMP-PAEK membranes with IEC a range of 1.1-1.9 mequiv. g^{-1} were obtained via copolymerization and subsequent sulfonation. Firstly, the SMP-PAEK membranes containing 0.6, 0.7, 0.8 and 0.9 molar percentage of pendant methoxyphenyl group (SMP-PAEK -60, -70, -80 and -90) were prepared by nucleophilic polycondensation reaction (Scheme 1). The polymerization reaction proceeded smoothly, and there is no evident crosslinking was observed while the system was carefully purged with nitrogen and the temperature as well was controlled by oil bath. The viscosity values of polymers showed that high molecular weight polymers ($\eta_{sp/C}$ > 1.5 dL/g) were obtained. The chemical structure of sulfonated methoxyphenyl containing poly(arylene ether ketone) (SMP-PAEK) was confirmed by Fourier transform infrared (FT-IR) and ^{1}H NMR spectroscopies. As shown in **Fig. 1**, the FT-IR spectroscopy confirmed the presence of sulfonated groups. In comparison with unsulfonated polymers, new absorption bands around 1030 and 1078, 1095 cm^{-1} arise from symmetric and asymmetric stretching vibrations of sulfonic groups in sulfonated polymers. The ^{1}H NMR spectrum of MP-PAEK-60 and SMP-PAEK-60 are shown in **Fig. 2.** The simple NMR patterns of both spectra indicated the hydrogen at the para-position of the pendant group was fully substituted by a sulfonic acid group. It is also supported by the accurate peak integration values in ^{1}H NMR, which correspond to a fully substituted polymer. Furthermore, unsulfonated and sulfonated polymers were prepared in a common solvent and were soluble in DMSO-d_6. The spectra shows signal positions and peak intensities appear obvious changes, which indicate full substitution had occurred. All the peaks were well assigned to the supposed chemical structure. As expected, the unsulfonated polymer had a proton signal in ortho-position of methoxyl group (peak k, δ = 6.8 ppm) and there is no signal in the sulfonated polymer at the exactly same chemical shift. In contrast to the unsulfonated polymers, the sulfonated polymer appears a sulfonic acid group signal (peak j, δ = 8.26 ppm), which was fully characterized to ascertain the presence of a sulfonic acid group and also its exact position on the phenyl ring as well. and the peak g moved to low chemical shift, so The sulfonated site was identified as on the para-position of the pendant phenyl ring, the peak of the proton next to carbonyl(C=O) was δ = 7.6 ppm above and ether linkage (—O—) was in the range of δ =6.6-7.4 ppm. The signal of H atom in methoxyl group appeared at low chemical shift and the signal of H atom in meta-position of –CO– groups appeared at high chemical shift, which confirmed the formation of the sulfonated polymer.

The viscosity of polymers were measured by using an Ubbelohde Viscometer. As shown in **Table 1**, the intrinsic viscosity values of SMP-PAEK are higher than 1.5 dL/g, which indicated that the polymers had high molecular weight. The DS of SMP-PAEK were determined by elemental analysis, which was close to the theoretical value and confirmed that the polymers were sulfonated to various degrees of sulfonation from 0.6 to 0.9. The targeted IEC values are compared with the values determined experimentally by acid-base titration and elemental analysis in **Table 1**. It can be noticed that, in general, the experimental IEC values were close to the anticipated values. Furthermore, the IEC determined by elemental analysis was close to the values determined by titration. The above results proved again that proton conductive groups, –SO_3H could be introduced into the specific position of polymer via the post-sulfonation methods. Consequently, the DS values of this family of polymers could be well controlled by their structural makeup. Thus, the DS could be expected from the ratios of feed ratios of monomers, which is a considerable advantage over the method controlled by reaction time and temperature.

3.2 Thermal stability

Polymer materials usually were operated below the glass transition temperature (T_g) in order to maintain their good mechanical strength, The operation temperature of the high temperature fuel cell thus demands PEM materials with high T_g. DSC measurements were carried out to investigate the T_g of polymer membranes with different methoxy group contents (**Fig. 3**). Only one transition temperature was found in the DSC curve and lower than the decomposition temperature for all the polymers, which indicated they possess amorphous nature. For unsulfonated polymers, T_g values were in the range of 142-148 °C which was mainly attributed to their rigid chain rigidity. In general, T_g values shifted to higher temperatures after sulfonation because of the introduction of polar sulfonic acid groups. In Fig. 3, the T_g values were more obvious than the sulfonated polymers, due to the molecular interaction of sulfonic acid groups. The TGA curve of MP-PAEK-80 (**Fig. 4**) showed a single step thermal degradation at 420 °C, which indicated that the incorporation of 6FBPA did not forfeit thermal stability due to the strong C-F bond. The TGA experiments were performed at a heating rate of 10 °C min^{-1} in the air since the air environment is similar to fuel cell operating conditions. In contrast to unsulfonated MP-PAEK, the SMP-PAEK exhibited two distinct thermal degradation steps. The SMP-PAEK polymers showed the 5% weight loss high temperature and onset weight loss temperature were higher than 300 °C (**Table 1**) and 220 °C (**Fig. 4**), respectively. The high initial thermal degradation temperature of SMP-PAEK indicates their thermal stability may be adequate for application in PEMFC.

3.3 Water uptake and Swelling ratio

Water uptake and dimensional swelling ratio of PEMs are closely related to IEC, proton conductivity, dimensional stability and mechanical strength. On one hand, the water within the membrane provides a carrier for the proton transportation to maintain high proton conductivity, on the other hand, excessive water uptake in a PEM leads to unacceptable dimensional change, which could lead to lack of durability when the membrane was incorporated into a membrane electrode assembly (MEA). Therefore, the preparation of sulfonated polymers with moderate water uptakes and dimensional stability is one of the critical demands for their application as PEMs. The water uptake and swelling ratio of the SMP-PAEK membranes were tested and list in **Table 2**. The SMP-PAEK-60 and -70 membranes exhibited moderate water uptake and lower swelling ratio, that comparable to Nafion 117 at all test range of temperature in water. Which indicate that the SMP-PAEK membrane with low IEC vale is suitable for operating in high humidity condition for PEM materials. Although the SMP-PAEK-80 and -90 membranes exhibited a poor dimensional stability in water (Fig. 5), they may have good water remain ability at low humidity and high temperature. Water uptake of the SMP-PAEK membranes were measured at 80 °C as a function of RH (**Fig. 6**). All four membranes showed an increase water sorption as a function of humidity below 80% RH, and membranes had similar water uptake at lower to moderate RH values while showing a much greater increase in absorbed water above 80% RH. The SMP-PAEK-80 and -90 have higher water uptake in low humidity. This indicated SMP-PAEK membranes with high IEC value tend exposed to low humidity conditions.

3.4 Proton conductivity

The proton conductivities of the SMP-PAEK membranes at different temperatures and RH are presented in Table 2. As expected, the SMP-PAEK membranes showed very high proton conductivity, which were higher than that of Nafion 117 in water. In addition, the proton conductivity of SMP-PAEK with comparable IEC values were much higher than that of literature reported copolymers Me-6F-SPEEK and Ph-6FA-SPEEK, and even higher than two orders of magnitude at room temperature [40]. As shown in **Fig.7** (a), the conductivities of all the SMP-PAEK increased with temperature increased except SMP-PAEK-90 membrane. The reason was that the SMP-PAEK-90 membrane absorbed too much water at high temperature, result in ion concentration being diluted in the membrane, on the other hand, the microstructure of polymer was destroyed due to membrane excess swelling. As shown in **Fig. 7** (b), the conductivities of SMP-PAEK-80, 90 and Nafion117 Membrane were measured in a range of 30-98% RH at 80 °C, the conductivity increased with RH increased, which indicated that the presence of additional water enhanced conduction by either vehicular or Grotthuss mechanism. The conductivities of SMP-PAEK-90 and -80 membrane were not much different from Nafion117 at different RH, which indicated the membranes weren't dehydrated under low humidity conditions. Conductivity values of the SMP-PAEK membranes are acceptable to obtain good fuel cell performances.

3.5 Single cell performance

Fig. 8 shows the polarization and power density curves of the single cells assembled with the SMP-PAEK-80 membrane under a fully hydrated condition at room temperature. The current density of the single cells was measured to be 235 mA/cm^2 at a 0.36 voltage (V). In addition, the maximum power density of the membranes was measured to be 83.7 mW/cm^2. It was expected that SMP-PAEK-80 showed higher power density due to its higher proton conductivity. The result demonstrates that our membranes have good potential to be an alternative PEM for fuel cell applications.

3.6 Structure analysis by SAXS

SAXS experiments are widely used to investigate the nanostructure of ionomers. The morphological differences between Nafion membranes and conventionally sulfonated hydrocarbon aromatic membranes have previously been extensively discussed by Kreuer and Jannasch on the basis of SAXS data.[26] Furthermore, concentrated sulfonated polymers are anticipated to have an enhanced phase separation, owing to their longer hydrophobic segment and sulfonic acid clusters. In this work, the SAXS experiment of hydrated SMP-PAEK membranes was performed at room temperature in the q range of 0.02–7 nm^{-1}. As shown in **Fig. 9**, all the sulfonated polymers display a distinct ionomer peak as well as Nafion 117. The characteristic separation lengths of these ionomers were calculated and included in **Fig. 9**. Obviously, d value of the SMP-PAEK was similar to Nafion 117, which suggested a connected ionic domain existed in membranes. IEC and the d values of SMP-PAEK may have a correlation. For IEC values ranging from 1.24 to 1.84 $meq.g^{-1}$, the d values decrease from 3.6 nm for SMP-PAEK-60 to 2.8 nm for SMP-PAEK-90. Hence, the ionic domain possesses a larger area in SMP-PAEK membranes with a higher IEC value. This is consistent with the result of water uptake behaviour and conductivity.

3.7 Mechanical properties

Good mechanical property of the PEMs is one of necessary demands for their applications in either the anhydrous or swelled states. As shown in **Table 3**, the mechanical properties of membranes were detected in dry and swelled state. The tensile stress at maximum load and elongation at break of SMP-PAEK membranes are 30.0-32.4 MPa and120-171% in dry state, respectively, and 20.5-32.7 MPa and 103-123% in swelled state, respectively. As a result, the tensile strength of membranes were higher than Nafion 117 membrane, due to the SMP-PAEK membranes have higher rigid segments. In addition, the elongations at break of SMP-PAEK are higher than general SPAEK as literature has reported, which indicate their flexibility and high molecular weight. The mechanical properties results demonstrate that the membranes were strong and flexible materials in either dry or wet states, which would be of great advantage taking highly pressurized MEA into account for PEMFC applications.

4. Conclusions

A series of SMP-PAEK were successfully synthesized via a postsulfonation approach under a mild reaction condition, leading to structurally well-defined sulfonated polymers that would normally be achieved only by a copolymerization route. Controlled substituted sites and the degree of sulfonation were realized by using quantities of difluoride monomer. The structure of SMP-PAEKwas confirmed by ^{1}H NMR and FT-IR instrument.The tough and transparent polymer membrane was prepared by solution casting method, exhibited excellent mechanical properties and high proton conductivities. The tensile stress at maximum load and elongation at break of these membranes are 30.0-32.4 MPa and 120-171% in dry state, respectively. The proton conductivities of these membranes are higher than that of Nafion 117 in water. Especially the SMP-PAEK with IEC of 1.62 mequiv/g exhibited the highest proton conductivity of 294 mS/cm at 80 °C in water; and SMP-PAEK with IEC of 1.83 mequiv/g exhibited suitable proton conductivities in different relative humidity (30~98%) at 80 ^{o}C, which is higher than Nafion 117. The clear micro-phase separation morphology was observed by SAXS, which is a powerful evidence to explain their high conductive behavior. The current density of the SMP-PAEK-80 membrane was measured to be 235 mA/cm^2 at 0.36 voltage (V) under fully hydrated conditions at room temperature. These results suggest that the SMP-PAEK membranes have great potential as a candidate membrane for PEMFC applications

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Table 1. Some properties of the SMP-PAEK

SMP-PAEK	^{a}DS	IEC (mequiv/g)			$Td_{(5\%)}$	$\eta_{sp/c}$
		IEC_{Target}	^{a}IEC	^{b}IEC	(^{o}C)	(dL/g)
SMP-PAEK-90	0.88	1.88	1.84	1.83	309	1.87
SMP-PAEK-80	0.79	1.66	1.64	1.62	316	1.75
SMP-PAEK-70	0.70	1.44	1.43	1.41	324	1.70
SMP-PAEK-60	0.61	1.22	1.24	1.18	341	1.55

^{a}: Elemental analysis result. b: Titration test result.

Table 2. Water uptake, swelling ratio and proton conductivity of the SMP-PAEK

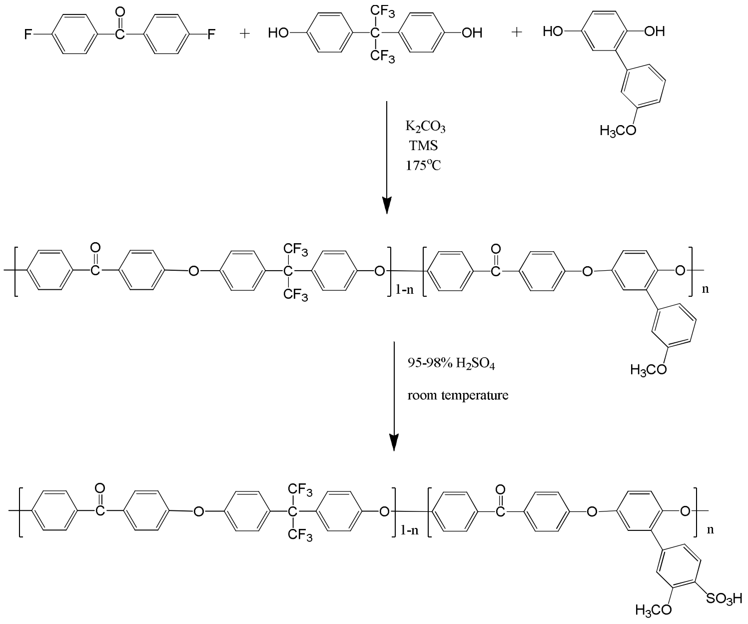
Polymer	Water uptake (Wt%)			Swelling ratio (L%)			Conductivity (mS/cm)		
	^{a}RT	^{a}80 ^{o}C	^{b}80 ^{o}C	^{a}RT	^{a}80 ^{o}C	^{b}80 ^{o}C	^{a}RT	^{a}80 ^{o}C	^{b}80 ^{o}C
SMP-PAEK-90	124	670	31.9	31.7	90.5	11.4	251	240	110
SMP-PAEK-80	60	208	27.5	19.4	56.2	9.2	184	294	71
SMP-PAEK-70	49	128	25.5	15.3	38.6	8.3	141	264	-
SMP-PAEK-60	37	69	23.7	11.1	21.7	5.2	114	230	-
Nafion 117	19.2	29.5	-	13.1	20.2	-	53	120	100

^{a}: in water. ^{b}: in 80% relative humidity.

Table 3. Mechanical properties of the SMP-PAEK-x in the anhydrous and swelled states

x	Tensile strength (MPa)		Elongation at break (%)	
	dry	wet	dry	wet

90	31.2	24.4	120	105
80	33.7	25.4	136	123
70	30.0	20.5	171	103
60	32.4	32.7	169	104



Scheme 1 Synthesis of the SMP-PAEK by post sulfonation method

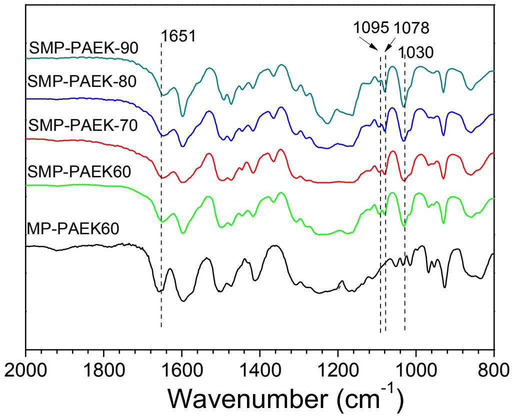


Fig. 1. FT-IR spectra of the MP-PAEK and SMP-PAEK

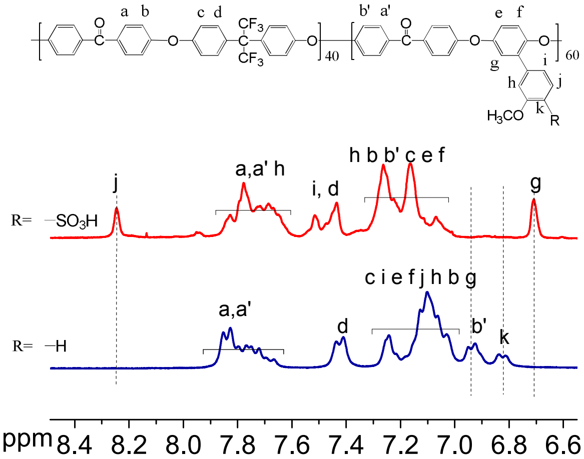


Fig. 2. ^{1}H NMR spectrum of MP-PAEK-60 and SMP-PAEK-60 (DMSO-d_6 as solvent)

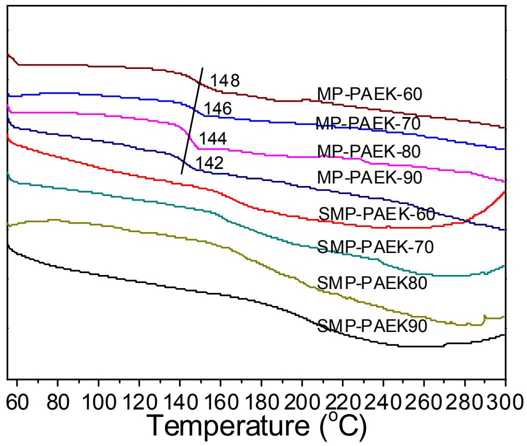


Fig. 3. DSC curve of the MP-PAEK and SMP-PAEK

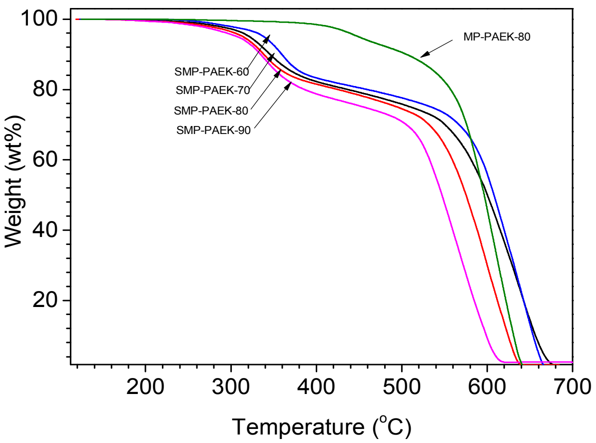


Fig. 4. TGA curve of the MP-PAEK and SMP-PAEK

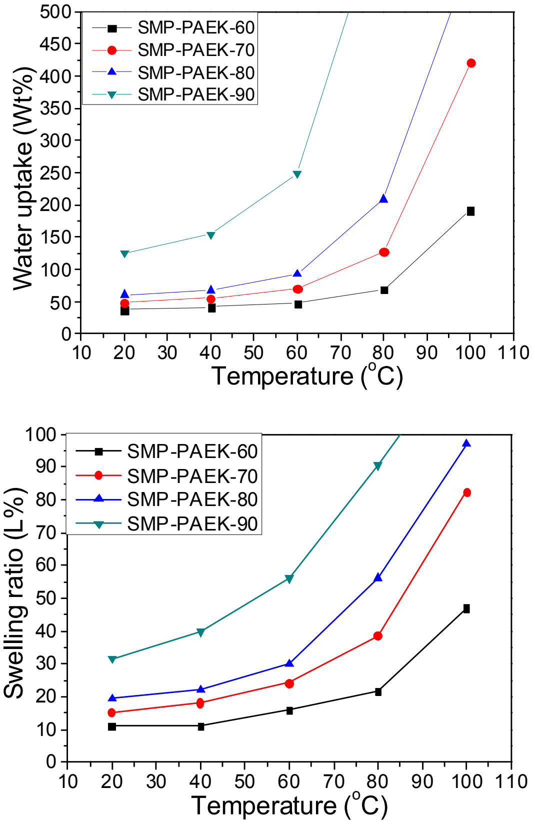


Fig. 5. Water uptake and Water swelling ratio of the SMP-PAEK as a function of temperature

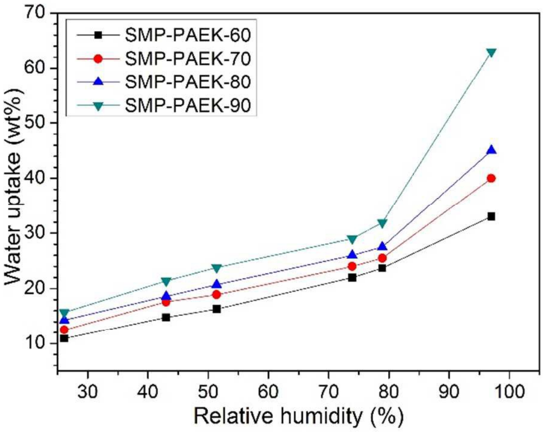
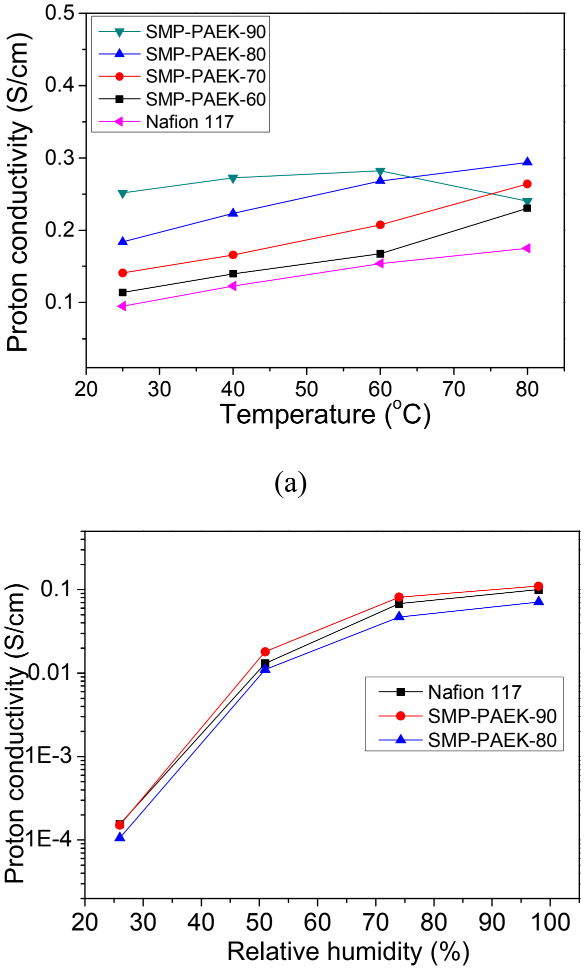


Fig. 6. Water uptakes of SMP-PAEK membranes as a function of RH at 80 ◦C



(a)

(b)

Fig. 7. Proton conductivity of the SMP-PAEK and Nafion 117 (a) as a function of temperature in water, (b) as a function of RH at 80 ◦C

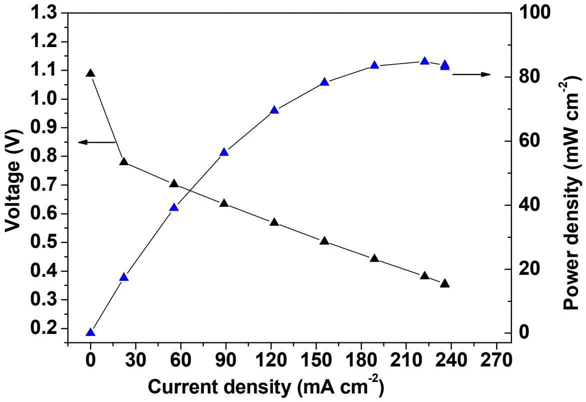


Fig. 8 PEMFC single cell performance of the SMP-PAEK-80 membranes under a fully hydrated condition at 80 °C

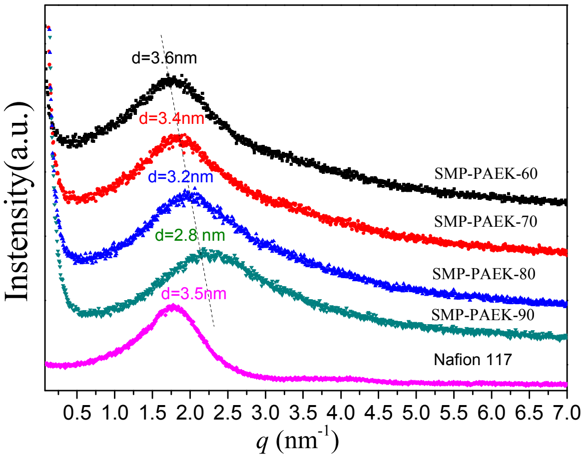


Fig. 9. The SAXS profiles of the SMP-PAEK and Nafion 117

Graphical abstract

“High proton conductivity sulfonated methoxyphenyl-containing poly(arylene ether ketone) for proton exchange membrane”

The polyelectrolyte membrane based on sulfonated methoxyphenyl-containing poly(arylene ether ketone) (SMP-PAEK) were obtained. Which exhibited suitable proton conductivities and excellent mechanical properties when immersed in water.